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Regio- and stereospecific assembly of dispiro-[indoline-3,3′-pyrrolizine-1′,5″-thiazolidines] from simple precursors using a one-pot procedure: synthesis, spectroscopic and structural characterization, and a proposed mechanism of formation

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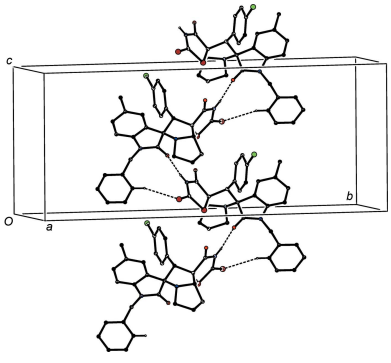
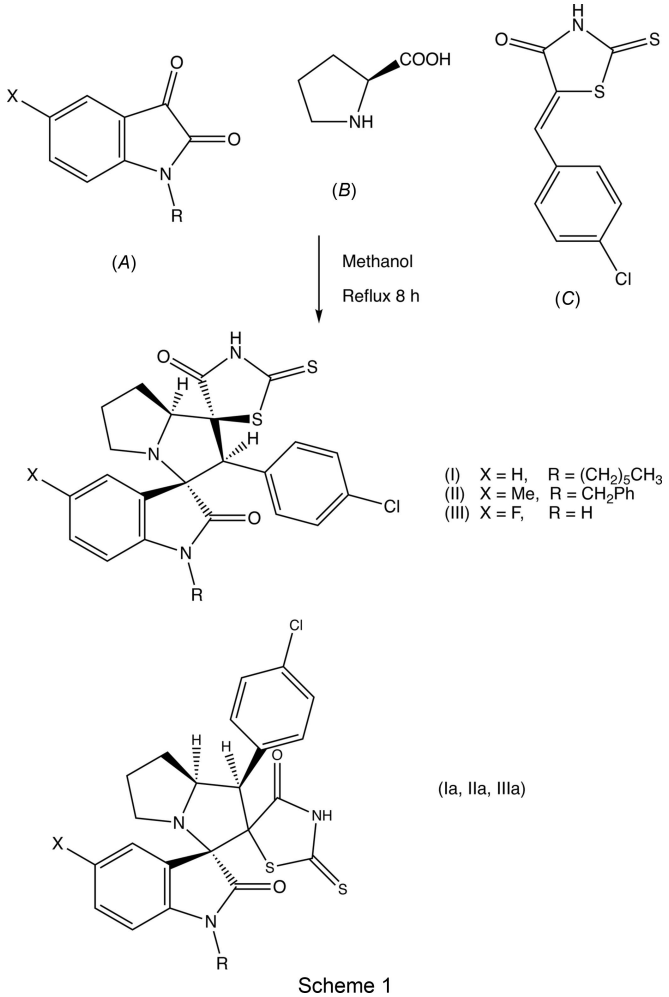
The synthesis and characterization of three new dispiro[indoline-3,3′-pyrrolizine-1′,5″-thiazolidine] compounds are reported, together with the crystal structures of two of them. (3*RS*,1′*SR*,2′*SR*,7a′*SR*)-2′-(4-Chlorophenyl)-1-hexyl-2″-sulfanylidene-5′,6′,7′,7a′-tetrahydro-2′*H*-dispiro[indoline-3,3′-pyrrolizine-1′,5″-thiazolidine]-2,4″-dione, $C_{28}H_{30}ClN_3O_2S_2$, (I), (3*RS*,1′*SR*,2′*SR*,7a′*SR*)-2′-(4-chlorophenyl)-1-benzyl-5-methyl-2″-sulfanylidene-5′,6′,7′,7a′-tetrahydro-2′*H*-dispiro[indoline-3,3′-pyrrolizine-1′,5″-thiazolidine]-2,4″-dione, $C_{30}H_{26}ClN_3O_2S_2$, (II), and (3*RS*,1′*SR*,2′*SR*,7a′*SR*)-2′-(4-chlorophenyl)-5-fluoro-2″-sulfanylidene-5′,6′,7′,7a′-tetrahydro-2′*H*-dispiro[indoline-3,3′-pyrrolizine-1′,5″-thiazolidine]-2,4″-dione, $C_{22}H_{17}ClFN_3O_2S_2$, (III), were each isolated as a single regioisomer using a one-pot reaction involving L-proline, a substituted isatin and (*Z*)-5-(4-chlorobenzylidene)-2-sulfanylidenethiazolidin-4-one [5-(4-chlorobenzylidene)rhodanine]. The compositions of (I)–(III) were established by elemental analysis, complemented by high-resolution mass spectrometry in the case of (I); their constitutions, including the definition of the regiochemistry, were established using NMR spectroscopy, and the relative configurations at the four stereogenic centres were established using single-crystal X-ray structure analysis. A possible reaction mechanism for the formation of (I)–(III) is proposed, based on the detailed stereochemistry. The molecules of (I) are linked into simple chains by a single N—H···N hydrogen bond, those of (II) are linked into a chain of rings by a combination of N—H···O and C—H···S=C hydrogen bonds, and those of (III) are linked into sheets by a combination of N—H···N and N—H···S=C hydrogen bonds.

1. Introduction

An attractive approach to the production of new organic compounds exhibiting broad-spectrum biological activity, for agricultural and pharmaceutical applications, is to combine in the same molecule two or more pharmacophores of proven efficacy. We report here on the synthesis, characterization and structure of a new heterocyclic system containing three such units, namely, the spiro-oxindole, pyrrolizine and rhodanine (2-sulfanylidenethiazolidin-4-one) units. Spiro-oxindoles are an important class of alkaloids derived from indole that are widely distributed in nature, including examples such as elacomine [(2′*S*,3*R*)-6-hydroxy-2′-(2-methylpropyl)spiro[1*H*-indole-3,3′-pyrrolidine]-2-one], horsfiline [(3*R*)-5-methoxy-1′-methylspiro[1*H*-indole-3,3′-pyrrolidine]-2-one] rhynchophylline [methyl (7β,16*E*,20α)-16-(methoxymethylene)-2-oxocorynoxan-17-oate] and spirotryprostatin {(3*S*,3′*S*,5′a*S*,10′a*S*)-6-



methoxy-3′-(2-methylprop-1-enyl)spiro[1*H*-indole-3,2′-3,5a,6,-7,8,10a-hexahydro-1*H*-dipyrrolo[1,2-*c*:1′,4′-*f*]pyrazine]-2,5′,10′-trione}, and compounds of this type exhibit a wide range of biological activity, including antibacterial, antifungal, antioxidant and antitumour activity (Russel, 2010). In addition, pyrrolizines have been found to be promising scaffolds for anticancer drugs (Belal & El-Gendy, 2014), while compounds derived from rhodanine have been found to exhibit outstanding levels of antibacterial and antifungal activity (Sortino *et al.*, 2007; Tomasić & Masic, 2009). Hence, the synthesis of new compounds containing all three of these molecular fragments, *i.e.* spiro-oxoindole, pyrrolizine and rhodanine, is essential, and an efficient route to such compounds involves a 1,3-dipolar cycloaddition reaction between an appropriate derivative of isatin (1*H*-indole-2,3-dione), an amino acid and an electron-deficient alkene (Ponnala *et al.*, 2006; Liu *et al.*, 2011).



Scheme 1

Accordingly, we report here the synthesis and characterization of three examples, namely, (3*RS*,1′*SR*,2′*SR*,7a′*SR*)-2′-(4-chlorophenyl)-1-hexyl-2″-sulfanylidene-5′,6′,7′,7a′-tetrahydro-2′*H*-dispiro[indoline-3,3′-pyrrolizine-1′,5″-thiazolidine]-2,4″-dione, (I), (3*RS*,1′*SR*,2′*SR*,7a′*SR*)-2′-(4-chlorophenyl)-1-benzyl-5-methyl-2″-sulfanylidene-5′,6′,7′,7a′-tetrahydro-2′*H*-dispiro[indoline-3,3′-pyrrolizine-1′,5″-thiazolidine]-2,4″-dione, (II), and (3*RS*,1′*SR*,2′*SR*,7a′*SR*)-2′-(4-chlorophenyl)-5-fluoro-2″-sulfanylidene-5′,6′,7′,7a′-tetrahydro-2′*H*-dispiro[indoline-3,3′-pyrrolizine-1′,5″-thiazolidine]-2,4″-dione, (III), along with the structures of compounds (I) and (II) (Figs. 1 and 2). The compounds were synthesized, as the sole isolated product in each case, in a one-pot procedure involving the reaction between an isatin, (*A*) [1-hexylisatin for (I), *N*-benzyl-5-methylisatin for (II) and 5-fluoroisatin for (III)], L-proline, (*B*), and the electron-deficient alkene (*Z*)-5-(4-chlorobenzylidene)-2-sulfanylidenethiazolidin-4-one [5-(4-chlorobenzylidene)rhodanine], (*C*) (Scheme 1). Analysis of the NMR spectra showed which regioisomer had been isolated, while the crystal structure analyses for (I) and (II) established the relative stereochemistry at the four contiguous stereogenic centres at the atoms labelled here as C13, C21, C22 and C27*A* (Figs. 1 and 2), which correspond to the chemical sites C3, C1′, C2′ and C7a′, respectively, as defined in §2.3 below.

2. Experimental

2.1. Synthesis and crystallization

For the synthesis of compounds (I)–(III), a solution containing equimolar quantities (0.39 mmol of each reactant) of L-proline, (*Z*)-5-(4-chlorobenzylidene)-2-sulfanylidenethiazolidin-4-one and the appropriate isatin in methanol (120 ml) was heated under reflux for 8 h, after which time monitoring using thin-layer chromatography (TLC) indicated that the reactions were complete. Each solution was then allowed to cool to ambient temperature and the resulting solid product was collected by filtration. Crystals suitable for single-crystal X-ray diffraction were selected directly from the synthetic products.

2.2. Analytical data

2.2.1. Compound (I). Yield 52%, m.p. > 570 K. NMR (DMSO-d_6): δ(^{1}H) 0.76–0.90 (*m*, 3H), 1.10–1.32 (*m*, 6H), 1.40–1.54 (*m*, 2H), 1.75–1.89 (*m*, 1H), 1.89–1.99 (*m*, 1H), 1.99–2.13 (*m*, 2H), 2.41–2.48 (*m*, 1H), 2.52–2.57 (*m*, 1H), 3.51–3.69 (*m*, 2H), 4.42 (*t*, *J* = 7.22 Hz, 1H, H-7a′), 4.64 (*s*, 1H, H-2′), 6.86 (*d*, *J* = 7.61 Hz, 1H, H-7), 7.04 (*t*, *J* = 7.52 Hz, 1H, H-6), 7.14 (*d*, *J* = 8.59 Hz, 2H, H$_o$), 7.18 (*t*, *J* = 7.71 Hz, 1H, H-5), 7.25 (*d*, *J* = 8.59 Hz, 2H, H$_m$), 7.49 (*d*, *J* = 7.22 Hz, 1H, H-4), 13.21 (*br s*, 1H, NH-3″); δ(^{13}C) 14.3 (CH_3), 22.5 (CH_2), 26.6 (CH_2), 27.4 (CH_2), 28.1 (CH_2), 30.0 (CH_2), 31.3 (CH_2), 40.0 (CH_2), 47.3 (CH_2), 65.3 (C-2′), 74.3 (C-spiro), 74.9 (C-7a′), 75.1 (C-spiro), 109.5 (C-7), 123.6 (C-6), 124.0 (C-4), 128.7 (C$_m$), 129.0 (C), 129.9 (C-5), 130.5 (C), 132.4 (C$_o$), 134.0 (C), 142.9 (C), 176.1 (N—C═O), 179.6 (N—C═O), 203.9 (C═S). MS–ESI (*m*/*z*) found for [*M* + H]$^+$ 540.1543, $C_{28}H_{31}ClN_3O_2S_2$ has an exact mass of 540.1546. MS–EI (70 eV) *m*/*z* (%) 499 (6), 284 [100, M^+ − 4-Cl-(C_6H_4)–CHC–$CONHCS_2$], 255 {27, [4-Cl-(C_6H_4)–CHC–$CONHCS_2$]}, 217 (17), 168 (82), 133 (33), 118 (25), 89 (38). Analysis (%) found: C 62.4, H 5.5, N 7.7; $C_{28}H_{30}ClN_3O_2S_2$ requires: C 62.3, H 5.6, N 7.8.

2.2.2. Compound (II). Yield 50%, m.p. > 570 K. NMR (DMSO-d_6): δ(^{1}H) 1.84 (*dt*, *J* = 19.1, 17.4, 9.1 Hz, 1H, H-6′), 1.92–2.01 (*m*, 1H, H-7′), 2.02–2.14 (*m*, 2H, H-6′ & H-7′), 2.25 (*s*, 3H, 5-CH_3), 2.54–2.61 (*m*, 1H, H-5′), 4.43 (*t*, *J* = 7.2 Hz, 1H,

Table 1
Experimental details.

For both structures: $Z = 4$. Experiments were carried out at 100 K with Mo $K\alpha$ radiation using a Bruker D8 Venture diffractometer. Absorption was corrected for by multi-scan methods (*SADABS*; Bruker, 2016). H atoms were treated by a mixture of independent and constrained refinement.

	(I)	(II)
Crystal data		
Chemical formula	$C_{28}H_{30}ClN_3O_2S_2$	$C_{30}H_{26}ClN_3O_2S_2$
M_r	540.12	560.11
Crystal system, space group	Monoclinic, $P2_1/c$	Orthorhombic, $Pna2_1$
a, b, c (Å)	14.1669 (5), 10.7145 (3), 17.1350 (5)	8.2419 (2), 28.0429 (6), 11.5843 (3)
α, β, γ (°)	90, 98.654 (1), 90	90, 90, 90
V (Å^3)	2571.33 (14)	2677.44 (11)
μ (mm^{-1})	0.34	0.33
Crystal size (mm)	0.18 × 0.11 × 0.05	0.34 × 0.18 × 0.12
Data collection		
T_{min}, T_{max}	0.906, 0.983	0.917, 0.961
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	58781, 6390, 5580	26105, 6574, 6425
R_{int}	0.049	0.038
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.667	0.667
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.032, 0.075, 1.03	0.026, 0.064, 1.05
No. of reflections	6390	6574
No. of parameters	329	347
No. of restraints	0	1
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.47, −0.41	0.37, −0.27
Absolute structure	–	Flack x determined using 2956 quotients $[(I^+) - (I^-)]/[(I^+) + (I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	–	0.050 (19)

Computer programs: *APEX3* (Bruker, 2018), *SAINT* (Bruker, 2017), *SHELXT2014* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*) and *PLATON* (Spek, 2020).

H-7a′), 4.67 (*s*, 1H, H-2′), 4.80 (*d*, *J* = 15.5 Hz, 1H, NC*H*H), 4.86 (*d*, *J* = 15.5 Hz, 1H, NCH*H*), 6.69 (*d*, *J* = 8.00 Hz, 1H), 6.93 (*d*, *J* = 7.61 Hz, 1H), 7.10 (*d*, *J* = 8.94 Hz, 2H), 7.14 (*d*, *J* = 8.76 Hz, 2H), 7.21 (*dd*, *J* = 7.55, 1.98 Hz, 2H), 7.27–7.37 (*m*, 4H), 13.22 (*br s*, 1H, H-3′′); $\delta(^{13}C)$ 21.1 (5-CH_3), 28.2 (CH_2), 30.0 (CH_2), 43.5 (N—CH_2), 47.2 (CH_2), 65.2 (C-2′), 74.4 (C-spiro), 74.9 (C-7a′), 75.2 (C-spiro), 109.8 (CH), 124.8 (CH), 128.0 (CH), 128.2 (CH), 128.8 (CH), 129.0 (C), 129.1 (CH), 130.1 (CH), 130.5 (C), 132.3 (CH), 133.1 (C), 133.9 (C), 136.3 (C), 140.1 (C), 176.2 (N—C═O), 179.6 (N—C═O), 203.8 (C═S). MS–EI (70 eV) *m*/*z* (%) 539 (5), 304 {60, M^+ − 4-Cl-(C_6H_4)–CHC–$CONHCS_2$], 255 {4, [4-Cl-(C_6H_4)–CHC–CO-$NHCS_2$]}, 236 (16), 213 (10), 168 (100), 133 (40), 123 (8), 91 [75, $(C_7H_7)^+$], 89 (55). Analysis (%) found: C 64.4, H 4.6, N 7.4; $C_{30}H_{26}ClN_3O_2S_2$ requires: C 64.3, H 4.7, N 7.5.

2.2.3. Compound (III). Yield 49%, m.p. > 570 K. NMR (DMSO-d_6): $\delta(^1H)$ 1.76–1.89 (*m*, 1H, H-6′), 1.89–1.99 (*m*, 1H, H-7′), 2.00–2.12 (*m*, 2H, H-6′ & H-7′), 2.53–2.64 (*m*, 1H, H-5′), 4.41 (*t*, *J* = 7.3 Hz, 1H, H-7a′), 4.66 (*s*, 1H, H-2′), 6.62 (*dd*, *J* = 8.4, 4.3 Hz, 1H), 6.92 (*ddd*, *J* = 11.1, 8.7, 2.7 Hz, 1H), 7.24 (*d*, *J* = 8.6, Hz, 2H, H_o), 7.31 (*d*, *J* = 8.6 Hz, 2H, H_m), 7.37 (*dd*, *J* = 8.1, 2.7 Hz, 1H), 10.73 (*s*, 1H, NH), 13.19 (*br s*, 1H, NH-1), 13.19 (*br s*, 1H, H-3′′); $\delta(^{13}C)$ 28.2 (CH_2), 29.9 (CH_2), 47.3 (CH_2), 65.0 (C-2′), 74.3 (C-spiro), 75.0 (C-7a′), 75.9 (C-spiro), 111.2 (*d*, J_{CF} = 7.3 Hz, C), 112.2 (*d*, J_{CF} = 24.8 Hz, CH), 116.2 (*d*, J_{CF} = 23.3 Hz, CH), 128.9 (CH), 130.6 (C), 131.7 (*d*, J_{CF} = 7.3 Hz, C—N), 132.3 (CH), 134.1 (C), 137.9 (C), 157.8 (C), 159.0 (*d*, J_{CF} = 237 Hz, C—F), 160.2 (C), 178.3 (N—C═O), 179.5 (N—C═O), 204.0 (C═S). MS–EI (70 eV) *m*/*z* (%) 473 (1.3, M^+), 368 (3), 355 (6), 255 [6, 4-Cl-(C_6H_4)-CHC-$CONHCS_2$], 218 {20, M^+ − [4-Cl-(C_6H_4)–CHC–$CONHCS_2$]}, 215 (51), 168 (17), 160 (20), 127 (35), 111 (18), 97 (37), 81 (49), 55 (75), 44 (100). Analysis (%) found: C 55.7, H 3.7, N 8.8; $C_{22}H_{17}Cl$-$FN_3O_2S_2$ requires: C 55.8, H 3.6, N 8.9.

2.3. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The atom labelling for the central dispiro unit is based on the systematic chemical numbering, following the convention used previously (Quiroga *et al.*, 2017); thus, the atoms with chemical locants N1, C2 and so on are labelled here as N11, C12, *etc.*; those atoms with chemical locants such as C1′, C2′ and so on are labelled here as C21, C22, *etc.*; and those atoms with chemical locants such as S1′′, C2′′ and so on are labelled here as S31, C32, *etc.* All other chemical fragments are treated as substituents on the central dispiro unit. All H atoms were located in difference maps. H atoms bonded to C atoms were subsequently treated as riding atoms in geometrically idealized positions, with C—H = 0.95 (aromatic), 0.98 (CH_3), 0.99 (CH_2) or 1.00 Å (aliphatic C—H), and with $U_{iso}(H) = kU_{eq}(C)$, where k = 1.5 for the methyl groups, which were permitted to rotate but not to tilt, and 1.2 for all other H atoms bonded to C atoms. For the H atoms bonded to N atoms, the atomic coordinates were refined with $U_{iso}(H) = 1.2U_{eq}(N)$, giving an N—H distance of 0.862 (17) Å in (I) and 0.77 (3) Å in (II). For compound (II), the correct orientation of the structure with

respect to the polar-axis direction was calculated by means of the Flack x parameter (Flack, 1983), with x = 0.050 (19) as calculated (Parsons *et al.*, 2013) using 2956 quotients of the type $[(I^+) - (I^-)]/[(I^+) + (I^-)]$.

3. Results and discussion

Compounds (I)–(III) (Scheme 1) were each isolated as a single stereoisomer in yields of 53% for (I), 49% for (II) and 50% for (III). For all three products, the compositions were established by elemental analysis, complemented by high-resolution mass spectrometry in the case of (I) (§2.1). The ^{1}H and ^{13}C NMR spectra contained all the signals expected for the proposed formulations, and the regioselectivity of the reactions leading to the products was established by analysis of the ^{1}H spectra; it is necessary here to discuss only the analysis for (I), as those for (II) and (III) follow entirely similar lines. For (I), the signal from the proton H2′ bonded to atom C2′ (atom C22 in the crystallographic labeling scheme; see Fig. 1 and §2.2) was observed as a singlet at δ 4.64, while the signal for H7a′ bonded to C7a′ (C27*A*) was observed as a triplet (J = 7.22 Hz) at δ 4.42. These two signals indicate the formation of the pyrrolizine in (I), singly substituted at position C2′ and doubly substituted at positions C1′ and C3′, so confirming the identity of regioisomer (I) (Scheme 1 and Fig. 1). Had the alternative regioisomer (I*a*) been formed, the appearance of these two pyrrolizine signals would have been different; that for atom H7a′ would have been a doublet of triplets and, crucially, that for atom H1′ would have appeared as a doublet, rather than the singlet actually observed. Entirely similar remarks apply to the spectra of compounds (II) and (III) but, in addition, five of the signals in the ^{13}C NMR spectrum of (III) exhibit coupling to the ^{19}F nucleus at position 5, namely, those at δ 159.0 for C5, 131.7 for C7, 116.2 and 112.2 for C4 and C6, and 111.2 for C3*A*; the four-bond coupling to atom C7*A* is too small to be resolved.

Although the regiochemistry of the synthetic reactions can be deduced from the NMR data, it is not possible to establish from these data the relative stereochemistry of all four stereogenic centres, but this is readily achieved by crystal structure analysis. The space groups for compounds (I) and (II) (Table 1) show that they have both crystallized as racemic mixtures and, for each compound, the reference molecule was selected as that having the *R* configuration at atom C13 (Figs. 1 and 2); on this basis, the configuration at each of atoms C21, C22 and C27*A* is *S*, with these atoms corresponding, respectively, to locants C3, C1′, C2′ and C7a′ in the chemical numbering scheme, so that the overall configuration of these compounds is (3*RS*,1′*SR*,2′*SR*,3′*SR*).

Based on earlier work (Pardasani *et al.*, 2003; Quiroga *et al.*, 2017), a reaction sequence can be proposed which commences with nucleophilic addition of the proline component (*B*) to the isatin (*A*) (Scheme 1) to form the intermediate (*D*) (Scheme 2), followed by sequential cyclodehydration to give (*E*) and decarboxylation to form the key azomethine intermediate (*F*). This intermediate then undergoes a 1,3-dipolar cycloaddition with the electron-deficient alkene (*C*) to form

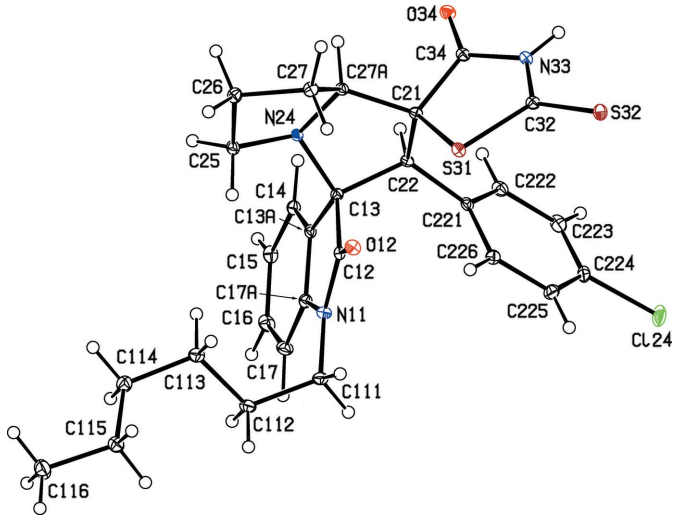


Figure 1
The molecular structure of the (3*R*,1′*S*,2′*S*,7a′*S*) enantiomer of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

the products (I)–(III). The alternative orientation of the alkene relative to the azomethine in the addition reaction would give the products (I*a*)–(III*a*) with transposed chlorophenyl and rhodanine units, but these have not been detected. Thus, the negative pole of intermediate (*F*) has coupled to the heterocyclic end of the alkenic double bond, adjacent to the carbonyl group, rather than to the chlorophenyl end. Neither of the components in the cycloaddition reaction step contains any stereogenic centres, and there are no reagents present which could induce enantioselectivity; hence the products are formed as racemic mixtures. These each contain four contiguous stereogenic centres, so that whichever of these centres is formed first, it appears to exert strong control over the formation of all the others. In the transition state leading to the formation of the products (I)–(III), the reactants can

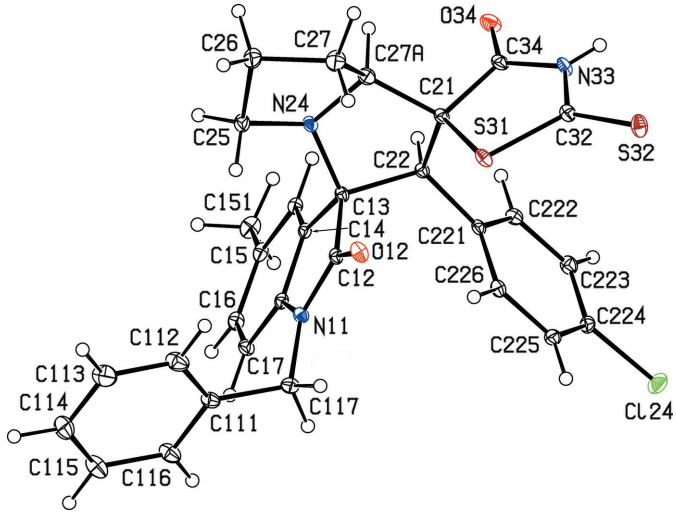
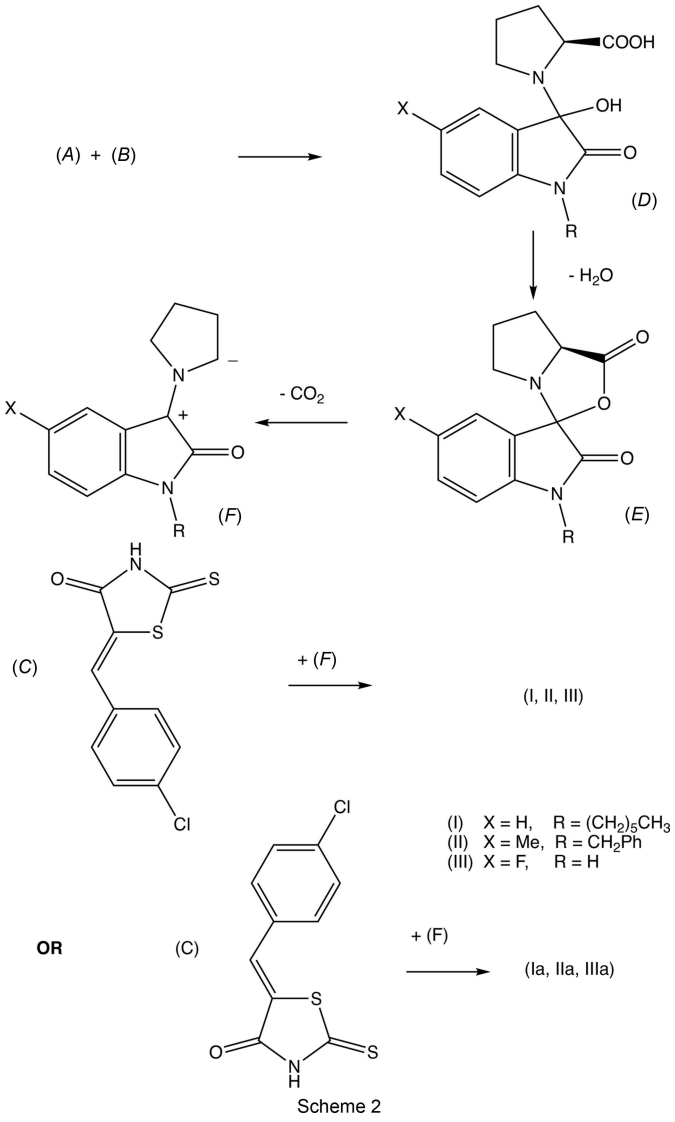


Figure 2
The molecular structure of the (3*R*,1′*S*,2′*S*,7a′*S*) enantiomer of compound (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

approach one another in two orientations: the *endo* transition state, in which the Cl atom is remote from the aryl ring of the isatin unit, leads to the observed (3*RS*,1′*SR*,2′*SR*,3′*SR*) stereochemistry, whereas the alternative *exo* transition state, with the Cl atom close to the aryl ring of the isatin, would lead to the alternative (3*RS*,1′*RS*,2′*RS*,3′*RS*) stereochemistry, which is not observed. The choice of the transition state in this step is presumably determined by the minimization of steric hindrance. Hence this proposed reaction mechanism can account for both the regiochemistry and for the relative stereochemistry at the four stereogenic centres.



Scheme 2

Within the molecules of (I) and (II), the rhodanine rings are almost planar, with r.m.s. deviations from the mean planes of the five ring atoms of 0.0573 Å in (I) and 0.0210 Å in (II). However, the rings containing atoms C22 and C25 (Figs. 1 and 2) both adopt half-chair conformations, as indicated by the ring-puckering parameters (Cremer & Pople, 1975) shown in Table 2. For an idealized half-chair conformation, the value of φ_2 is (36k + 18)°, where k represents an integer (Boeyens, 1978). Here the rings denoted *A* (Table 2) are twisted about a line joining atom C27*A* to the mid-point of the C13—C22 bond, while the rings denoted *B* are twisted about a line joining atom N24 to the mid-point of the C26—C27 bond.

Table 2
Ring-puckering parameters (Å, °).

Parameters for rings *A* and *B* are calculated for the atom sequences N24–C13–C22–C21–C27*A* and N24–C25–C26–C27–C27*A*, respectively. Data for (III) are available in the supporting information.

Ring *A*	(I)	(II)	(III)
Q_2	0.4311 (13)	0.411 (2)	0.424 (6)
φ_2	55.57 (17)	61.9 (3)	54.2 (8)
Ring *B*	**(I)**	**(II)**	**(III)**
Q_2	0.4103 (14)	0.416 (3)	0.390 (7)
φ_2	270.63 (18)	269.1 (3)	272.3 (9)

Overall, therefore, the composition of compounds (I)–(III) has been determined; the constitutions, including the regiochemistry, have been established from the NMR spectra and the relative configurations of the stereogenic centres, and the conformations of the nonplanar rings in (I) and (II) have been established from the X-ray structure analyses. We have also investigated the crystal structure of compound (III). Despite repeated attempts at crystallization, this compound consistently formed tightly-packed clusters of very thin lath-like crystals, and the resulting diffraction data and the structure deduced from it is of somewhat indifferent quality (see supporting information). After conventional refinement of (III), the resulting difference map contained several significant electron-density maxima, but no chemically plausible solvent model could be developed from these peaks. Accordingly, SQUEEZE (Spek, 2015) was applied and the

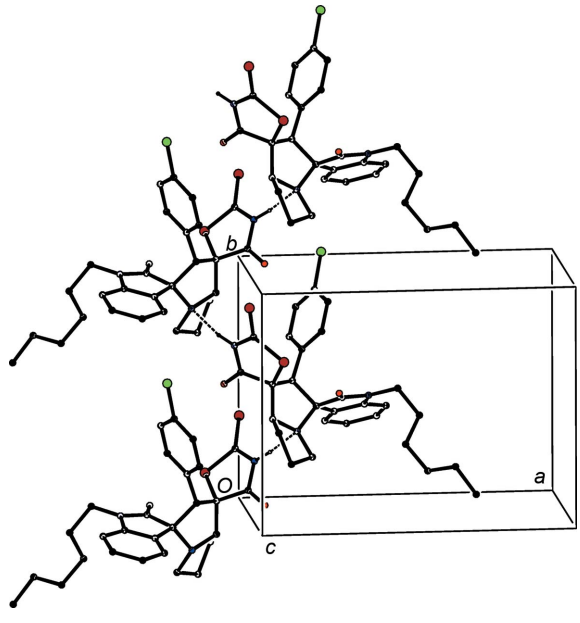


Figure 3
Part of the crystal structure of compound (I), showing the formation of a hydrogen-bonded $C(6)$ chain running parallel to [010]. Hydrogen bonds are drawn as dashed lines and, for the sake of clarity, H atoms bonded to C atoms have all been omitted.

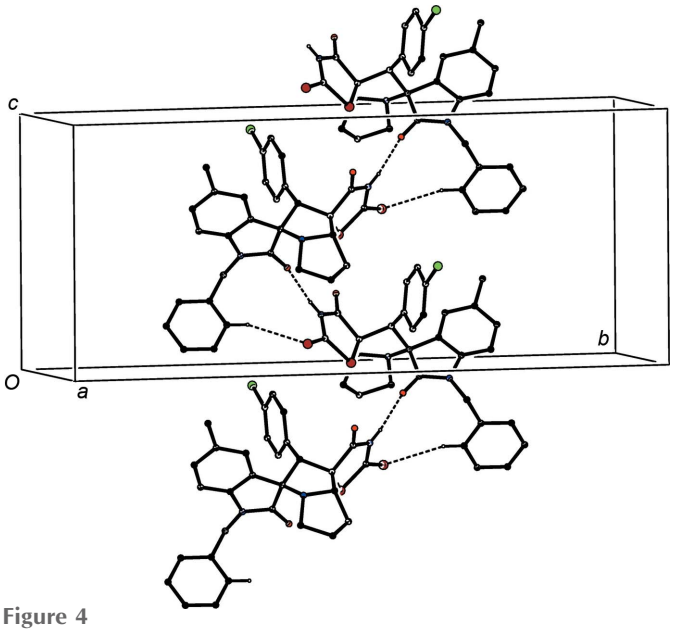


Figure 4
Part of the crystal structure of compound (II), showing the formation of a hydrogen-bonded $C(8)C(12)[R_2^2(11)]$ chain of rings running parallel to [010]. Hydrogen bonds are drawn as dashed lines and, for the sake of clarity, H atoms bonded to C atoms have all been omitted.

refinement using this modified data set established that the constitution and configuration of (III) are the same as those for compounds (I) and (II), and that the conformations of the type *A* and *B* rings are also very similar to those in (I) and (II)

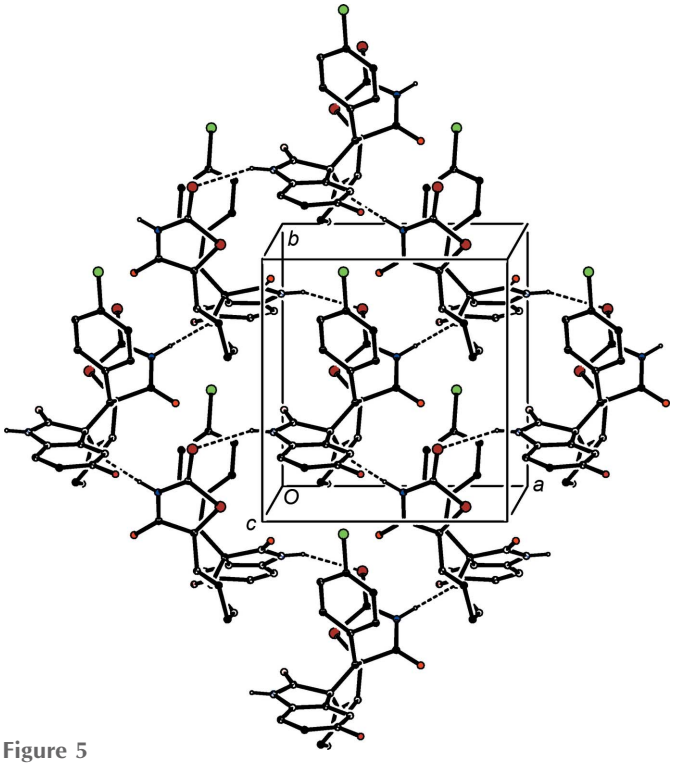


Figure 5
Part of the crystal structure of compound (III), showing the formation of a hydrogen-bonded sheet of $R_4^4(24)$ rings; see supporting information for full details. Hydrogen bonds are drawn as dashed line lines and, for the sake of clarity, H atoms bonded to C atoms have all been omitted.

Table 3
Hydrogen-bond parameters (Å, °).

The data for (III) are available in the supporting information.

	D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
(I)	N33—H33···N24^{i}	0.863 (17)	2.079 (17)	2.8933 (15)	157.2 (16)
(II)	N33—H33···O12^{ii}	0.77 (3)	2.05 (3)	2.811 (2)	170 (3)
	C112—H112···S32^{iii}	0.95	2.88	3.760 (3)	155
(III)	N11—H11···S32^{iv}	0.88	2.55	3.374 (5)	156
	N33—H33···N24^{v}	0.88	2.08	2.878 (7)	150

Symmetry codes: (i) $-x, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x+1, -y+1, z+\frac{1}{2}$; (iii) $-x+1, -y+1, z-\frac{1}{2}$; (iv) $-x, y-\frac{1}{2}, -z+\frac{1}{2}$; (v) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$.

(Table 2). However, the identity of the included solvent species remains undetermined.

The supramolecular assembly of both (I) and (II) is very simple. In compound (I), a single N—H···N hydrogen bond (Table 3) links molecules which are related by a 2_1 screw axis to form simple *C*(6) chains (Etter, 1990; Etter *et al.*, 1990; Bernstein *et al.*, 1995) running parallel to the [010] direction (Fig. 3), but there are no direction-specific interactions between adjacent chains. In compound (II), molecules which are related by a 2_1 screw axis are linked by a combination of one N—H···O hydrogen bond and one C—H···S═C hydrogen bond (Table 3). These two interactions, acting singly, give rise to *C*(8) and *C*(12) chains, respectively, while in combination they generate a $C(8)C(12)[R_2^2(11)]$ chain of rings (Fig. 4). There are no direction-specific interactions between adjacent chains. The crystal structure of (III) contains N—H···N and N—H···S hydrogen bonds (Table 3), which individually generate *C*(6) and *C*(9) chains, both running parallel to the [010] direction, and in combination these interactions generate a sheet of $R_4^4(24)$ rings lying parallel to (001) (Fig. 5).

A number of structures have been reported for spiro[indoline-3,3′-pyrrolizine] derivatives (Sarrafi & Alimohammadi, 2008*a*,*b*; Sathya *et al.*, 2012; Fathimunnisa *et al.*, 2015; Corres *et al.*, 2016), but often without any mention of either the relative or the absolute stereochemistry, despite the presence of multiple stereogenic centres.

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supporting information

Acta Cryst. (2020). C**76** [https://doi.org/10.1107/S2053229620009791]

Regio- and stereospecific assembly of dispiro[indoline-3,3′-pyrrolizine-1′,5′′-thiazolidines] from simple precursors using a one-pot procedure: synthesis, spectroscopic and structural characterization, and a proposed mechanism of formation

Pablo Romo, Jairo Quiroga, Justo Cobo and Christopher Glidewell

Computing details

For both structures, data collection: *APEX3* (Bruker, 2018); cell refinement: *SAINT*(Bruker, 2017); data reduction: *SAINT* (Bruker, 2017); program(s) used to solve structure: SHELXT2014 (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *PLATON* (Spek, 2020); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015b) and *PLATON* (Spek, 2020).

(3*RS*,1′*SR*,2′*SR*,7a′*SR*)-2′-(4-Chlorophenyl)-1-hexyl-2′′-sulfanylidene-5′,6′,7′,7a′-tetrahydro-2′*H*-dispiro[indoline-3,3′-pyrrolizine-1′,5′′-thiazolidine]-2,4′′-dione (I)

Crystal data

$C_{28}H_{30}ClN_3O_2S_2$
M_r = 540.12
Monoclinic, $P2_1/c$
a = 14.1669 (5) Å
b = 10.7145 (3) Å
c = 17.1350 (5) Å
β = 98.654 (1)°
V = 2571.33 (14) Å^3
Z = 4
$F(000)$ = 1136
D_x = 1.395 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 6390 reflections
θ = 2.3–28.3°
μ = 0.34 mm^{-1}
T = 100 K
Block, colourless
0.18 × 0.11 × 0.05 mm

Data collection

Bruker D8 Venture diffractometer
Radiation source: INCOATEC high brilliance microfocus sealed tube
Multilayer mirror monochromator
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2016)
T_{min} = 0.906, T_{max} = 0.983
58781 measured reflections
6390 independent reflections
5580 reflections with $I > 2\sigma(I)$
R_{int} = 0.049
θ_{max} = 28.3°, θ_{min} = 2.3°
h = −18→18
k = −14→14
l = −22→22

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.075
S = 1.03
6390 reflections

329 parameters
0 restraints
Primary atom site location: difference Fourier map
Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0261P)^2 + 1.9059P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.47$ e Å^{-3}
$\Delta\rho_{min} = -0.41$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
N11	0.38984 (8)	0.46405 (10)	0.32810 (6)	0.0124 (2)
C12	0.30350 (9)	0.46202 (11)	0.35416 (7)	0.0111 (2)
O12	0.28957 (7)	0.48958 (9)	0.42055 (5)	0.01425 (19)
C13	0.22665 (9)	0.41823 (12)	0.28497 (7)	0.0101 (2)
C13A	0.28767 (9)	0.38460 (12)	0.22290 (7)	0.0110 (2)
C14	0.26377 (9)	0.33426 (12)	0.14842 (8)	0.0132 (2)
H14	0.1993	0.3139	0.1286	0.016*
C15	0.33628 (10)	0.31370 (13)	0.10258 (8)	0.0155 (3)
H15	0.3213	0.2767	0.0518	0.019*
C16	0.42985 (10)	0.34706 (13)	0.13089 (8)	0.0174 (3)
H16	0.4780	0.3334	0.0988	0.021*
C17	0.45472 (10)	0.40035 (13)	0.20557 (8)	0.0162 (3)
H17	0.5186	0.4245	0.2245	0.019*
C17A	0.38255 (9)	0.41647 (12)	0.25075 (7)	0.0123 (2)
C21	0.08415 (9)	0.51746 (12)	0.32233 (7)	0.0103 (2)
C22	0.15215 (9)	0.52067 (11)	0.25754 (7)	0.0099 (2)
H22	0.1129	0.4856	0.2091	0.012*
N24	0.16385 (7)	0.31858 (10)	0.30627 (6)	0.0101 (2)
C25	0.20764 (9)	0.21899 (12)	0.36102 (7)	0.0130 (2)
H25A	0.2707	0.2458	0.3890	0.016*
H25B	0.2158	0.1409	0.3319	0.016*
C26	0.13670 (10)	0.20031 (12)	0.41911 (8)	0.0143 (3)
H26A	0.1692	0.1688	0.4705	0.017*
H26B	0.0856	0.1411	0.3978	0.017*
C27	0.09634 (9)	0.33176 (12)	0.42746 (7)	0.0137 (2)
H27A	0.0348	0.3291	0.4482	0.016*
H27B	0.1419	0.3851	0.4621	0.016*
C27A	0.08320 (9)	0.37667 (12)	0.34186 (7)	0.0109 (2)
H271	0.0220	0.3409	0.3142	0.013*
S31	0.11441 (2)	0.62162 (3)	0.40671 (2)	0.01185 (7)
C32	0.02013 (9)	0.72364 (12)	0.37629 (7)	0.0116 (2)
S32	0.00374 (2)	0.85216 (3)	0.42460 (2)	0.01431 (7)

N33	−0.03583 (8)	0.68025 (10)	0.31006 (6)	0.0121 (2)
H33	−0.0841 (12)	0.7206 (16)	0.2856 (10)	0.014*
C34	−0.01382 (9)	0.56458 (12)	0.28215 (7)	0.0112 (2)
O34	−0.06330 (7)	0.50921 (9)	0.23002 (5)	0.01482 (19)
C111	0.47900 (9)	0.49823 (13)	0.37816 (8)	0.0145 (3)
H11A	0.4638	0.5358	0.4276	0.017*
H11B	0.5121	0.5623	0.3507	0.017*
C112	0.54657 (9)	0.38780 (13)	0.39904 (8)	0.0151 (3)
H12A	0.5736	0.3630	0.3513	0.018*
H12B	0.6002	0.4153	0.4392	0.018*
C113	0.49993 (10)	0.27395 (13)	0.43052 (8)	0.0165 (3)
H13A	0.4452	0.2473	0.3912	0.020*
H13B	0.4749	0.2973	0.4794	0.020*
C114	0.56909 (10)	0.16447 (13)	0.44815 (8)	0.0179 (3)
H14A	0.5332	0.0914	0.4634	0.021*
H14B	0.5946	0.1425	0.3992	0.021*
C115	0.65276 (10)	0.18967 (13)	0.51338 (8)	0.0175 (3)
H15A	0.6277	0.2152	0.5619	0.021*
H15B	0.6911	0.2597	0.4972	0.021*
C116	0.71704 (11)	0.07583 (14)	0.53159 (9)	0.0237 (3)
H16A	0.7424	0.0505	0.4839	0.036*
H16B	0.6800	0.0071	0.5494	0.036*
H16C	0.7700	0.0968	0.5732	0.036*
C221	0.18456 (9)	0.64645 (12)	0.23251 (7)	0.0115 (2)
C222	0.15072 (10)	0.68746 (13)	0.15582 (8)	0.0153 (3)
H222	0.1120	0.6335	0.1204	0.018*
C223	0.17286 (10)	0.80581 (14)	0.13059 (8)	0.0187 (3)
H223	0.1498	0.8328	0.0784	0.022*
C224	0.22895 (10)	0.88346 (13)	0.18270 (9)	0.0185 (3)
Cl24	0.25285 (3)	1.03498 (3)	0.15442 (3)	0.02795 (10)
C225	0.26587 (10)	0.84461 (13)	0.25809 (9)	0.0179 (3)
H225	0.3056	0.8985	0.2928	0.021*
C226	0.24403 (9)	0.72571 (12)	0.28246 (8)	0.0145 (3)
H226	0.2700	0.6980	0.3339	0.017*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N11	0.0098 (5)	0.0146 (5)	0.0126 (5)	−0.0008 (4)	0.0012 (4)	−0.0001 (4)
C12	0.0104 (6)	0.0087 (5)	0.0140 (6)	0.0012 (4)	0.0009 (4)	0.0019 (4)
O12	0.0141 (4)	0.0166 (5)	0.0120 (4)	0.0010 (4)	0.0018 (3)	−0.0013 (3)
C13	0.0102 (6)	0.0101 (6)	0.0100 (5)	−0.0003 (4)	0.0020 (4)	0.0000 (4)
C13A	0.0114 (6)	0.0096 (6)	0.0127 (6)	0.0012 (4)	0.0038 (5)	0.0027 (4)
C14	0.0132 (6)	0.0124 (6)	0.0139 (6)	0.0004 (5)	0.0019 (5)	0.0017 (5)
C15	0.0193 (7)	0.0149 (6)	0.0129 (6)	0.0025 (5)	0.0049 (5)	0.0004 (5)
C16	0.0167 (7)	0.0202 (7)	0.0173 (6)	0.0037 (5)	0.0088 (5)	0.0022 (5)
C17	0.0117 (6)	0.0192 (7)	0.0185 (6)	0.0007 (5)	0.0046 (5)	0.0021 (5)
C17A	0.0123 (6)	0.0117 (6)	0.0132 (6)	0.0005 (5)	0.0026 (5)	0.0017 (5)

C21	0.0094 (6)	0.0121 (6)	0.0091 (5)	0.0000 (4)	0.0011 (4)	−0.0007 (4)
C22	0.0087 (5)	0.0116 (6)	0.0097 (5)	0.0004 (4)	0.0022 (4)	−0.0002 (4)
N24	0.0089 (5)	0.0100 (5)	0.0116 (5)	0.0004 (4)	0.0026 (4)	0.0015 (4)
C25	0.0126 (6)	0.0122 (6)	0.0140 (6)	0.0014 (5)	0.0018 (5)	0.0034 (5)
C26	0.0158 (6)	0.0140 (6)	0.0135 (6)	0.0001 (5)	0.0035 (5)	0.0032 (5)
C27	0.0148 (6)	0.0152 (6)	0.0121 (6)	0.0003 (5)	0.0049 (5)	0.0025 (5)
C27A	0.0096 (6)	0.0117 (6)	0.0116 (6)	0.0003 (5)	0.0026 (4)	0.0009 (4)
S31	0.01191 (14)	0.01336 (15)	0.00997 (14)	0.00198 (11)	0.00067 (11)	−0.00128 (11)
C32	0.0110 (6)	0.0138 (6)	0.0108 (5)	−0.0002 (5)	0.0040 (4)	0.0024 (4)
S32	0.01623 (16)	0.01289 (15)	0.01414 (15)	0.00173 (12)	0.00338 (12)	−0.00180 (11)
N33	0.0106 (5)	0.0126 (5)	0.0129 (5)	0.0022 (4)	0.0011 (4)	0.0006 (4)
C34	0.0105 (6)	0.0135 (6)	0.0102 (5)	0.0008 (5)	0.0039 (4)	0.0022 (4)
O34	0.0124 (4)	0.0169 (5)	0.0145 (4)	0.0005 (4)	0.0000 (3)	−0.0018 (4)
C111	0.0106 (6)	0.0158 (6)	0.0164 (6)	−0.0023 (5)	−0.0004 (5)	−0.0001 (5)
C112	0.0102 (6)	0.0183 (6)	0.0163 (6)	−0.0006 (5)	0.0006 (5)	0.0012 (5)
C113	0.0129 (6)	0.0173 (6)	0.0187 (6)	−0.0011 (5)	0.0001 (5)	0.0015 (5)
C114	0.0183 (7)	0.0151 (6)	0.0194 (7)	−0.0005 (5)	−0.0001 (5)	−0.0010 (5)
C115	0.0154 (6)	0.0173 (7)	0.0193 (7)	0.0012 (5)	0.0007 (5)	−0.0005 (5)
C116	0.0224 (7)	0.0212 (7)	0.0259 (7)	0.0057 (6)	−0.0014 (6)	0.0002 (6)
C221	0.0101 (6)	0.0116 (6)	0.0136 (6)	0.0023 (5)	0.0043 (5)	0.0009 (5)
C222	0.0134 (6)	0.0188 (7)	0.0143 (6)	0.0018 (5)	0.0046 (5)	0.0026 (5)
C223	0.0180 (7)	0.0208 (7)	0.0190 (7)	0.0048 (5)	0.0082 (5)	0.0080 (5)
C224	0.0167 (7)	0.0117 (6)	0.0305 (8)	0.0032 (5)	0.0144 (6)	0.0065 (5)
Cl24	0.0302 (2)	0.01309 (16)	0.0458 (2)	0.00390 (14)	0.02268 (17)	0.01029 (15)
C225	0.0158 (6)	0.0140 (6)	0.0251 (7)	−0.0020 (5)	0.0075 (5)	−0.0022 (5)
C226	0.0134 (6)	0.0143 (6)	0.0161 (6)	0.0003 (5)	0.0033 (5)	0.0009 (5)

Geometric parameters (Å, º)

N11—C12	1.3639 (16)	S31—C32	1.7438 (13)
N11—C17A	1.4093 (16)	C32—N33	1.3645 (16)
N11—C111	1.4627 (16)	C32—S32	1.6411 (13)
C12—O12	1.2198 (16)	N33—C34	1.3809 (17)
C12—C13	1.5566 (17)	N33—H33	0.862 (17)
C13—N24	1.4705 (16)	C34—O34	1.2053 (16)
C13—C13A	1.5115 (17)	C111—C112	1.5301 (18)
C13—C22	1.5460 (17)	C111—H11A	0.9900
C13A—C14	1.3800 (18)	C111—H11B	0.9900
C13A—C17A	1.3993 (18)	C112—C113	1.5241 (19)
C14—C15	1.4014 (18)	C112—H12A	0.9900
C14—H14	0.9500	C112—H12B	0.9900
C15—C16	1.388 (2)	C113—C114	1.5291 (19)
C15—H15	0.9500	C113—H13A	0.9900
C16—C17	1.3972 (19)	C113—H13B	0.9900
C16—H16	0.9500	C114—C115	1.5259 (19)
C17—C17A	1.3830 (18)	C114—H14A	0.9900
C17—H17	0.9500	C114—H14B	0.9900
C21—C34	1.5388 (17)	C115—C116	1.5261 (19)

C21—C27A	1.5457 (17)	C115—H15A	0.9900
C21—C22	1.5758 (17)	C115—H15B	0.9900
C21—S31	1.8258 (13)	C116—H16A	0.9800
C22—C221	1.5067 (17)	C116—H16B	0.9800
C22—H22	1.0000	C116—H16C	0.9800
N24—C25	1.4928 (16)	C221—C226	1.3951 (18)
N24—C27A	1.5080 (16)	C221—C222	1.4000 (18)
C25—C26	1.5304 (18)	C222—C223	1.3908 (19)
C25—H25A	0.9900	C222—H222	0.9500
C25—H25B	0.9900	C223—C224	1.381 (2)
C26—C27	1.5348 (18)	C223—H223	0.9500
C26—H26A	0.9900	C224—C225	1.383 (2)
C26—H26B	0.9900	C224—Cl24	1.7419 (14)
C27—C27A	1.5282 (17)	C225—C226	1.3899 (19)
C27—H27A	0.9900	C225—H225	0.9500
C27—H27B	0.9900	C226—H226	0.9500
C27A—H271	1.0000		

C12—N11—C17A	111.08 (10)	C27—C27A—H271	107.8
C12—N11—C111	123.36 (11)	C21—C27A—H271	107.8
C17A—N11—C111	125.22 (11)	C32—S31—C21	93.93 (6)
O12—C12—N11	125.48 (12)	N33—C32—S32	126.64 (10)
O12—C12—C13	126.20 (11)	N33—C32—S31	110.98 (9)
N11—C12—C13	108.32 (10)	S32—C32—S31	122.37 (8)
N24—C13—C13A	115.66 (10)	C32—N33—C34	117.43 (11)
N24—C13—C22	100.37 (9)	C32—N33—H33	123.5 (11)
C13A—C13—C22	113.07 (10)	C34—N33—H33	119.1 (11)
N24—C13—C12	114.19 (10)	O34—C34—N33	124.19 (12)
C13A—C13—C12	101.49 (10)	O34—C34—C21	123.71 (11)
C22—C13—C12	112.63 (10)	N33—C34—C21	112.03 (11)
C14—C13A—C17A	120.01 (12)	N11—C111—C112	113.47 (11)
C14—C13A—C13	131.08 (12)	N11—C111—H11A	108.9
C17A—C13A—C13	108.88 (11)	C112—C111—H11A	108.9
C13A—C14—C15	118.77 (12)	N11—C111—H11B	108.9
C13A—C14—H14	120.6	C112—C111—H11B	108.9
C15—C14—H14	120.6	H11A—C111—H11B	107.7
C16—C15—C14	120.38 (12)	C113—C112—C111	114.35 (11)
C16—C15—H15	119.8	C113—C112—H12A	108.7
C14—C15—H15	119.8	C111—C112—H12A	108.7
C15—C16—C17	121.42 (12)	C113—C112—H12B	108.7
C15—C16—H16	119.3	C111—C112—H12B	108.7
C17—C16—H16	119.3	H12A—C112—H12B	107.6
C17A—C17—C16	117.26 (13)	C112—C113—C114	112.63 (11)
C17A—C17—H17	121.4	C112—C113—H13A	109.1
C16—C17—H17	121.4	C114—C113—H13A	109.1
C17—C17A—C13A	122.12 (12)	C112—C113—H13B	109.1
C17—C17A—N11	128.02 (12)	C114—C113—H13B	109.1
C13A—C17A—N11	109.86 (11)	H13A—C113—H13B	107.8

C34—C21—C27A	112.36 (10)	C115—C114—C113	114.40 (11)
C34—C21—C22	106.47 (9)	C115—C114—H14A	108.7
C27A—C21—C22	101.54 (9)	C113—C114—H14A	108.7
C34—C21—S31	104.02 (8)	C115—C114—H14B	108.7
C27A—C21—S31	115.71 (8)	C113—C114—H14B	108.7
C22—C21—S31	116.68 (8)	H14A—C114—H14B	107.6
C221—C22—C13	119.88 (10)	C114—C115—C116	112.47 (12)
C221—C22—C21	117.70 (10)	C114—C115—H15A	109.1
C13—C22—C21	103.42 (9)	C116—C115—H15A	109.1
C221—C22—H22	104.7	C114—C115—H15B	109.1
C13—C22—H22	104.7	C116—C115—H15B	109.1
C21—C22—H22	104.7	H15A—C115—H15B	107.8
C13—N24—C25	117.73 (10)	C115—C116—H16A	109.5
C13—N24—C27A	108.92 (9)	C115—C116—H16B	109.5
C25—N24—C27A	108.02 (9)	H16A—C116—H16B	109.5
N24—C25—C26	104.52 (10)	C115—C116—H16C	109.5
N24—C25—H25A	110.8	H16A—C116—H16C	109.5
C26—C25—H25A	110.8	H16B—C116—H16C	109.5
N24—C25—H25B	110.8	C226—C221—C222	118.33 (12)
C26—C25—H25B	110.8	C226—C221—C22	123.48 (11)
H25A—C25—H25B	108.9	C222—C221—C22	118.16 (11)
C25—C26—C27	103.35 (10)	C223—C222—C221	121.11 (13)
C25—C26—H26A	111.1	C223—C222—H222	119.4
C27—C26—H26A	111.1	C221—C222—H222	119.4
C25—C26—H26B	111.1	C224—C223—C222	118.88 (13)
C27—C26—H26B	111.1	C224—C223—H223	120.6
H26A—C26—H26B	109.1	C222—C223—H223	120.6
C27A—C27—C26	101.12 (10)	C223—C224—C225	121.51 (13)
C27A—C27—H27A	111.5	C223—C224—Cl24	119.91 (11)
C26—C27—H27A	111.5	C225—C224—Cl24	118.58 (12)
C27A—C27—H27B	111.5	C224—C225—C226	119.11 (13)
C26—C27—H27B	111.5	C224—C225—H225	120.4
H27A—C27—H27B	109.4	C226—C225—H225	120.4
N24—C27A—C27	105.54 (10)	C225—C226—C221	120.99 (13)
N24—C27A—C21	106.46 (10)	C225—C226—H226	119.5
C27—C27A—C21	120.75 (11)	C221—C226—H226	119.5
N24—C27A—H271	107.8		

C17A—N11—C12—O12	174.79 (12)	C27A—N24—C25—C26	12.63 (13)
C111—N11—C12—O12	1.2 (2)	N24—C25—C26—C27	−34.02 (13)
C17A—N11—C12—C13	−5.00 (14)	C25—C26—C27—C27A	41.69 (12)
C111—N11—C12—C13	−178.62 (11)	C13—N24—C27A—C27	−115.28 (11)
O12—C12—C13—N24	−48.63 (17)	C25—N24—C27A—C27	13.68 (13)
N11—C12—C13—N24	131.16 (11)	C13—N24—C27A—C21	14.19 (12)
O12—C12—C13—C13A	−173.78 (12)	C25—N24—C27A—C21	143.14 (10)
N11—C12—C13—C13A	6.01 (13)	C26—C27—C27A—N24	−34.02 (12)
O12—C12—C13—C22	65.02 (16)	C26—C27—C27A—C21	−154.53 (11)
N11—C12—C13—C22	−115.19 (11)	C34—C21—C27A—N24	127.01 (10)

N24—C13—C13A—C14	52.65 (18)	C22—C21—C27A—N24	13.63 (12)
C22—C13—C13A—C14	−62.29 (17)	S31—C21—C27A—N24	−113.73 (9)
C12—C13—C13A—C14	176.81 (13)	C34—C21—C27A—C27	−112.93 (12)
N24—C13—C13A—C17A	−129.14 (11)	C22—C21—C27A—C27	133.69 (11)
C22—C13—C13A—C17A	115.91 (12)	S31—C21—C27A—C27	6.33 (15)
C12—C13—C13A—C17A	−4.98 (13)	C34—C21—S31—C32	−9.48 (9)
C17A—C13A—C14—C15	1.29 (19)	C27A—C21—S31—C32	−133.22 (9)
C13—C13A—C14—C15	179.33 (12)	C22—C21—S31—C32	107.42 (9)
C13A—C14—C15—C16	−1.9 (2)	C21—S31—C32—N33	3.99 (10)
C14—C15—C16—C17	0.7 (2)	C21—S31—C32—S32	−177.07 (8)
C15—C16—C17—C17A	1.1 (2)	S32—C32—N33—C34	−174.88 (10)
C16—C17—C17A—C13A	−1.8 (2)	S31—C32—N33—C34	4.00 (14)
C16—C17—C17A—N11	177.88 (13)	C32—N33—C34—O34	171.20 (12)
C14—C13A—C17A—C17	0.6 (2)	C32—N33—C34—C21	−11.88 (15)
C13—C13A—C17A—C17	−177.83 (12)	C27A—C21—C34—O34	−43.92 (16)
C14—C13A—C17A—N11	−179.13 (11)	C22—C21—C34—O34	66.39 (15)
C13—C13A—C17A—N11	2.43 (14)	S31—C21—C34—O34	−169.81 (11)
C12—N11—C17A—C17	−177.99 (13)	C27A—C21—C34—N33	139.14 (11)
C111—N11—C17A—C17	−4.5 (2)	C22—C21—C34—N33	−110.55 (11)
C12—N11—C17A—C13A	1.73 (15)	S31—C21—C34—N33	13.26 (12)
C111—N11—C17A—C13A	175.20 (11)	C12—N11—C111—C112	109.24 (14)
N24—C13—C22—C221	177.40 (10)	C17A—N11—C111—C112	−63.47 (16)
C13A—C13—C22—C221	−58.79 (15)	N11—C111—C112—C113	−49.81 (15)
C12—C13—C22—C221	55.56 (14)	C111—C112—C113—C114	178.19 (11)
N24—C13—C22—C21	43.91 (11)	C112—C113—C114—C115	63.75 (16)
C13A—C13—C22—C21	167.72 (10)	C113—C114—C115—C116	177.22 (12)
C12—C13—C22—C21	−77.93 (12)	C13—C22—C221—C226	−61.00 (16)
C34—C21—C22—C221	72.19 (13)	C21—C22—C221—C226	66.16 (16)
C27A—C21—C22—C221	−170.08 (10)	C13—C22—C221—C222	121.09 (13)
S31—C21—C22—C221	−43.35 (14)	C21—C22—C221—C222	−111.76 (13)
C34—C21—C22—C13	−153.08 (10)	C226—C221—C222—C223	−2.19 (19)
C27A—C21—C22—C13	−35.35 (11)	C22—C221—C222—C223	175.83 (12)
S31—C21—C22—C13	91.38 (10)	C221—C222—C223—C224	−0.2 (2)
C13A—C13—N24—C25	78.63 (13)	C222—C223—C224—C225	2.2 (2)
C22—C13—N24—C25	−159.37 (10)	C222—C223—C224—Cl24	−176.75 (10)
C12—C13—N24—C25	−38.63 (15)	C223—C224—C225—C226	−1.6 (2)
C13A—C13—N24—C27A	−158.03 (10)	Cl24—C224—C225—C226	177.35 (10)
C22—C13—N24—C27A	−36.03 (11)	C224—C225—C226—C221	−1.0 (2)
C12—C13—N24—C27A	84.71 (12)	C222—C221—C226—C225	2.80 (19)
C13—N24—C25—C26	136.43 (11)	C22—C221—C226—C225	−175.12 (12)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N33—H33···N24^{i}	0.863 (17)	2.079 (17)	2.8933 (15)	157.2 (16)

Symmetry code: (i) −*x*, *y*+1/2, −*z*+1/2.

(3*RS*,1′*SR*,2′*SR*,7a′*SR*)-2′-(4-Chlorophenyl)-1-\ benzyl-5-methyl-2′′-sulfanylidene-5′,6′,7′,7a′-tetrahydro-2′*H*-\ dispiro[indoline-3,3′-pyrrolizine-1′,5′′-thiazolidine]-2,4′′-dione (II)

Crystal data

$C_{30}H_{26}ClN_3O_2S_2$
$M_r = 560.11$
Orthorhombic, $Pna2_1$
$a = 8.2419$ (2) Å
$b = 28.0429$ (6) Å
$c = 11.5843$ (3) Å
$V = 2677.44$ (11) Å^3
$Z = 4$
$F(000) = 1168$
$D_x = 1.390$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3475 reflections
$\theta = 2.6$–$28.3°$
$\mu = 0.33$ mm^{-1}
$T = 100$ K
Needle, colourless
0.34 × 0.18 × 0.12 mm

Data collection

Bruker D8 Venture diffractometer
Radiation source: INCOATEC high brilliance microfocus sealed tube
Multilayer mirror monochromator
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2016)
$T_{min} = 0.917$, $T_{max} = 0.961$
26105 measured reflections
6574 independent reflections
6425 reflections with $I > 2\sigma(I)$
$R_{int} = 0.038$
$\theta_{max} = 28.3°$, $\theta_{min} = 2.6°$
$h = -10 \rightarrow 10$
$k = -37 \rightarrow 37$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.064$
$S = 1.05$
6574 reflections
347 parameters
1 restraint
Primary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0258P)^2 + 0.6579P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}
Absolute structure: Flack *x* determined using 2956 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013)
Absolute structure parameter: 0.050 (19)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
N11	0.4912 (2)	0.32585 (6)	0.44612 (14)	0.0133 (3)
C12	0.5345 (2)	0.37223 (7)	0.45503 (16)	0.0127 (4)
O12	0.48339 (19)	0.40480 (5)	0.39356 (13)	0.0175 (3)
C13	0.6598 (2)	0.37797 (7)	0.55441 (16)	0.0117 (3)
C13A	0.6735 (2)	0.32703 (6)	0.59682 (17)	0.0117 (3)
C14	0.7598 (2)	0.30824 (7)	0.68828 (17)	0.0142 (4)

H14	0.8264	0.3282	0.7345	0.017*
C15	0.7479 (3)	0.25932 (7)	0.71215 (17)	0.0159 (4)
C16	0.6508 (3)	0.23092 (7)	0.64225 (18)	0.0170 (4)
H16	0.6455	0.1977	0.6573	0.020*
C17	0.5605 (3)	0.24957 (7)	0.55039 (17)	0.0155 (4)
H17	0.4933	0.2298	0.5040	0.019*
C17A	0.5734 (2)	0.29796 (7)	0.53023 (17)	0.0128 (3)
C21	0.6449 (2)	0.46322 (6)	0.60016 (18)	0.0131 (3)
C22	0.6043 (2)	0.41280 (6)	0.65025 (16)	0.0118 (3)
H22	0.6857	0.4082	0.7132	0.014*
N24	0.8120 (2)	0.40002 (5)	0.52018 (15)	0.0141 (3)
C25	0.8828 (3)	0.38859 (7)	0.40651 (19)	0.0175 (4)
H25A	0.7981	0.3776	0.3521	0.021*
H25B	0.9668	0.3635	0.4136	0.021*
C26	0.9574 (3)	0.43573 (8)	0.3661 (2)	0.0223 (5)
H26A	0.9632	0.4373	0.2808	0.027*
H26B	1.0675	0.4402	0.3984	0.027*
C27	0.8383 (3)	0.47302 (8)	0.4141 (2)	0.0232 (4)
H27A	0.8884	0.5051	0.4180	0.028*
H27B	0.7379	0.4747	0.3674	0.028*
C27A	0.8052 (3)	0.45299 (7)	0.53427 (18)	0.0175 (4)
H271	0.8973	0.4626	0.5854	0.021*
S31	0.48214 (6)	0.49186 (2)	0.51754 (4)	0.01522 (10)
C32	0.4565 (2)	0.53771 (7)	0.61713 (17)	0.0151 (4)
S32	0.31832 (7)	0.57931 (2)	0.60451 (5)	0.02113 (11)
N33	0.5668 (2)	0.53414 (6)	0.70448 (15)	0.0163 (3)
H33	0.563 (3)	0.5524 (10)	0.754 (2)	0.020*
C34	0.6749 (3)	0.49665 (7)	0.70299 (18)	0.0157 (4)
O34	0.7779 (2)	0.48991 (5)	0.77459 (15)	0.0226 (3)
C117	0.3670 (3)	0.30773 (7)	0.36649 (18)	0.0168 (4)
H11A	0.3074	0.3351	0.3330	0.020*
H11B	0.2882	0.2883	0.4106	0.020*
C111	0.4359 (3)	0.27787 (7)	0.26955 (18)	0.0169 (4)
C112	0.5196 (3)	0.29919 (9)	0.1790 (2)	0.0250 (5)
H112	0.5347	0.3328	0.1783	0.030*
C113	0.5812 (3)	0.27172 (10)	0.0896 (2)	0.0311 (5)
H113	0.6375	0.2866	0.0278	0.037*
C114	0.5610 (3)	0.22266 (9)	0.0902 (2)	0.0294 (5)
H114	0.6053	0.2039	0.0297	0.035*
C115	0.4764 (3)	0.20114 (9)	0.1788 (2)	0.0283 (5)
H115	0.4612	0.1676	0.1788	0.034*
C116	0.4133 (3)	0.22872 (8)	0.26831 (19)	0.0226 (4)
H116	0.3544	0.2138	0.3289	0.027*
C151	0.8387 (3)	0.23761 (8)	0.81275 (19)	0.0217 (4)
H15A	0.7616	0.2219	0.8647	0.032*
H15B	0.8965	0.2628	0.8547	0.032*
H15C	0.9168	0.2141	0.7839	0.032*
C221	0.4429 (2)	0.40572 (7)	0.70937 (17)	0.0127 (4)

C222	0.4450 (3)	0.40064 (7)	0.82936 (18)	0.0154 (4)
H222	0.5459	0.4008	0.8690	0.019*
C223	0.3016 (3)	0.39527 (7)	0.89188 (18)	0.0178 (4)
H223	0.3042	0.3919	0.9735	0.021*
C224	0.1555 (3)	0.39493 (7)	0.83321 (19)	0.0165 (4)
Cl24	−0.02407 (6)	0.39020 (2)	0.91141 (5)	0.02411 (12)
C225	0.1491 (3)	0.39936 (7)	0.71405 (19)	0.0159 (4)
H225	0.0478	0.3988	0.6749	0.019*
C226	0.2935 (2)	0.40461 (7)	0.65266 (17)	0.0143 (4)
H226	0.2902	0.4075	0.5710	0.017*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N11	0.0154 (8)	0.0116 (7)	0.0129 (7)	−0.0001 (6)	0.0002 (6)	0.0002 (6)
C12	0.0149 (9)	0.0124 (9)	0.0108 (8)	0.0003 (7)	0.0023 (7)	−0.0010 (7)
O12	0.0266 (8)	0.0126 (6)	0.0133 (7)	0.0028 (6)	−0.0015 (6)	0.0020 (6)
C13	0.0150 (9)	0.0094 (8)	0.0107 (8)	0.0003 (7)	0.0013 (7)	0.0003 (7)
C13A	0.0123 (8)	0.0091 (7)	0.0138 (8)	0.0008 (6)	0.0032 (7)	0.0010 (7)
C14	0.0133 (9)	0.0142 (9)	0.0151 (9)	0.0015 (7)	0.0015 (7)	0.0002 (7)
C15	0.0149 (9)	0.0155 (9)	0.0174 (9)	0.0034 (7)	0.0048 (7)	0.0037 (7)
C16	0.0189 (10)	0.0118 (8)	0.0203 (9)	0.0012 (7)	0.0051 (8)	0.0030 (7)
C17	0.0178 (9)	0.0113 (9)	0.0173 (9)	−0.0017 (7)	0.0029 (7)	−0.0010 (7)
C17A	0.0130 (8)	0.0123 (8)	0.0131 (9)	0.0009 (7)	0.0031 (7)	0.0007 (7)
C21	0.0157 (9)	0.0092 (8)	0.0146 (8)	−0.0004 (6)	0.0002 (7)	−0.0001 (7)
C22	0.0142 (9)	0.0096 (7)	0.0116 (8)	−0.0003 (7)	0.0006 (7)	0.0003 (7)
N24	0.0174 (8)	0.0092 (7)	0.0158 (8)	−0.0017 (6)	0.0040 (7)	−0.0004 (6)
C25	0.0192 (10)	0.0149 (8)	0.0183 (9)	−0.0011 (7)	0.0065 (8)	−0.0008 (8)
C26	0.0240 (11)	0.0169 (10)	0.0260 (11)	−0.0019 (8)	0.0105 (9)	0.0018 (8)
C27	0.0257 (11)	0.0170 (9)	0.0268 (11)	−0.0009 (8)	0.0073 (9)	0.0045 (9)
C27A	0.0189 (10)	0.0114 (8)	0.0221 (10)	−0.0008 (7)	0.0017 (8)	0.0006 (7)
S31	0.0228 (2)	0.01031 (19)	0.0126 (2)	0.00093 (17)	−0.0033 (2)	−0.00054 (18)
C32	0.0185 (9)	0.0130 (8)	0.0138 (9)	−0.0004 (7)	0.0011 (8)	−0.0003 (7)
S32	0.0245 (3)	0.0197 (2)	0.0192 (2)	0.0089 (2)	−0.0018 (2)	−0.0011 (2)
N33	0.0218 (9)	0.0122 (8)	0.0148 (8)	0.0022 (7)	−0.0031 (7)	−0.0054 (6)
C34	0.0184 (10)	0.0104 (8)	0.0184 (9)	−0.0028 (7)	0.0000 (7)	−0.0007 (7)
O34	0.0232 (8)	0.0184 (7)	0.0263 (8)	0.0002 (6)	−0.0093 (7)	−0.0040 (6)
C117	0.0161 (10)	0.0174 (9)	0.0171 (9)	−0.0019 (8)	−0.0027 (7)	−0.0009 (7)
C111	0.0186 (10)	0.0185 (10)	0.0138 (9)	−0.0028 (8)	−0.0036 (8)	−0.0014 (8)
C112	0.0319 (12)	0.0241 (11)	0.0189 (10)	−0.0090 (10)	0.0009 (9)	0.0002 (9)
C113	0.0370 (14)	0.0384 (13)	0.0180 (11)	−0.0126 (11)	0.0064 (10)	−0.0036 (10)
C114	0.0336 (13)	0.0346 (13)	0.0201 (11)	−0.0001 (10)	0.0006 (10)	−0.0107 (10)
C115	0.0393 (14)	0.0222 (11)	0.0233 (11)	−0.0012 (10)	−0.0029 (10)	−0.0057 (9)
C116	0.0317 (12)	0.0193 (10)	0.0168 (9)	−0.0055 (9)	−0.0005 (9)	−0.0008 (8)
C151	0.0217 (10)	0.0202 (10)	0.0231 (10)	0.0042 (8)	0.0007 (9)	0.0094 (8)
C221	0.0161 (10)	0.0083 (8)	0.0137 (9)	−0.0002 (7)	0.0016 (7)	−0.0011 (7)
C222	0.0174 (9)	0.0147 (9)	0.0142 (9)	−0.0009 (7)	−0.0016 (7)	−0.0002 (7)
C223	0.0226 (10)	0.0177 (9)	0.0130 (9)	−0.0015 (8)	0.0026 (8)	−0.0010 (7)

C224	0.0172 (9)	0.0125 (9)	0.0200 (9)	−0.0009 (7)	0.0066 (8)	−0.0003 (7)
Cl24	0.0185 (2)	0.0305 (3)	0.0234 (3)	−0.0019 (2)	0.0078 (2)	0.0009 (2)
C225	0.0147 (10)	0.0130 (9)	0.0200 (9)	0.0000 (7)	−0.0006 (8)	−0.0003 (7)
C226	0.0183 (10)	0.0128 (8)	0.0117 (8)	0.0012 (7)	0.0003 (7)	−0.0004 (7)

Geometric parameters (Å, º)

N11—C12	1.353 (2)	C27A—H271	1.0000
N11—C17A	1.421 (2)	S31—C32	1.740 (2)
N11—C117	1.469 (3)	C32—N33	1.364 (3)
C12—O12	1.232 (2)	C32—S32	1.637 (2)
C12—C13	1.555 (3)	N33—C34	1.378 (3)
C13—N24	1.454 (2)	N33—H33	0.77 (3)
C13—C13A	1.515 (2)	C34—O34	1.202 (3)
C13—C22	1.548 (3)	C117—C111	1.511 (3)
C13A—C14	1.381 (3)	C117—H11A	0.9900
C13A—C17A	1.393 (3)	C117—H11B	0.9900
C14—C15	1.403 (3)	C111—C112	1.391 (3)
C14—H14	0.9500	C111—C116	1.391 (3)
C15—C16	1.389 (3)	C112—C113	1.386 (3)
C15—C151	1.513 (3)	C112—H112	0.9500
C16—C17	1.400 (3)	C113—C114	1.386 (4)
C16—H16	0.9500	C113—H113	0.9500
C17—C17A	1.381 (3)	C114—C115	1.379 (4)
C17—H17	0.9500	C114—H114	0.9500
C21—C34	1.536 (3)	C115—C116	1.395 (3)
C21—C27A	1.552 (3)	C115—H115	0.9500
C21—C22	1.565 (3)	C116—H116	0.9500
C21—S31	1.833 (2)	C151—H15A	0.9800
C22—C221	1.509 (3)	C151—H15B	0.9800
C22—H22	1.0000	C151—H15C	0.9800
N24—C25	1.476 (3)	C221—C226	1.396 (3)
N24—C27A	1.495 (2)	C221—C222	1.397 (3)
C25—C26	1.531 (3)	C222—C223	1.394 (3)
C25—H25A	0.9900	C222—H222	0.9500
C25—H25B	0.9900	C223—C224	1.383 (3)
C26—C27	1.539 (3)	C223—H223	0.9500
C26—H26A	0.9900	C224—C225	1.387 (3)
C26—H26B	0.9900	C224—Cl24	1.740 (2)
C27—C27A	1.525 (3)	C225—C226	1.395 (3)
C27—H27A	0.9900	C225—H225	0.9500
C27—H27B	0.9900	C226—H226	0.9500
C12—N11—C17A	110.57 (16)	N24—C27A—C21	105.61 (15)
C12—N11—C117	124.35 (17)	C27—C27A—C21	122.20 (17)
C17A—N11—C117	124.92 (16)	N24—C27A—H271	107.7
O12—C12—N11	125.35 (18)	C27—C27A—H271	107.7
O12—C12—C13	125.31 (17)	C21—C27A—H271	107.7

N11—C12—C13	109.34 (16)	C32—S31—C21	93.81 (9)
N24—C13—C13A	115.15 (16)	N33—C32—S32	125.62 (15)
N24—C13—C22	100.50 (15)	N33—C32—S31	110.89 (14)
C13A—C13—C22	112.62 (15)	S32—C32—S31	123.49 (12)
N24—C13—C12	114.53 (16)	C32—N33—C34	118.52 (17)
C13A—C13—C12	101.07 (15)	C32—N33—H33	119 (2)
C22—C13—C12	113.60 (15)	C34—N33—H33	123 (2)
C14—C13A—C17A	120.46 (17)	O34—C34—N33	124.60 (19)
C14—C13A—C13	130.33 (18)	O34—C34—C21	123.56 (19)
C17A—C13A—C13	109.15 (17)	N33—C34—C21	111.82 (17)
C13A—C14—C15	119.23 (18)	N11—C117—C111	113.35 (17)
C13A—C14—H14	120.4	N11—C117—H11A	108.9
C15—C14—H14	120.4	C111—C117—H11A	108.9
C16—C15—C14	119.09 (18)	N11—C117—H11B	108.9
C16—C15—C151	120.21 (18)	C111—C117—H11B	108.9
C14—C15—C151	120.70 (19)	H11A—C117—H11B	107.7
C15—C16—C17	122.34 (18)	C112—C111—C116	119.0 (2)
C15—C16—H16	118.8	C112—C111—C117	120.59 (19)
C17—C16—H16	118.8	C116—C111—C117	120.42 (19)
C17A—C17—C16	117.06 (19)	C113—C112—C111	120.4 (2)
C17A—C17—H17	121.5	C113—C112—H112	119.8
C16—C17—H17	121.5	C111—C112—H112	119.8
C17—C17A—C13A	121.79 (18)	C114—C113—C112	120.3 (2)
C17—C17A—N11	128.32 (18)	C114—C113—H113	119.9
C13A—C17A—N11	109.87 (16)	C112—C113—H113	119.9
C34—C21—C27A	110.94 (16)	C115—C114—C113	119.9 (2)
C34—C21—C22	107.36 (16)	C115—C114—H114	120.0
C27A—C21—C22	101.39 (14)	C113—C114—H114	120.0
C34—C21—S31	104.79 (13)	C114—C115—C116	119.9 (2)
C27A—C21—S31	116.55 (14)	C114—C115—H115	120.0
C22—C21—S31	115.64 (13)	C116—C115—H115	120.0
C221—C22—C13	120.19 (16)	C111—C116—C115	120.5 (2)
C221—C22—C21	118.42 (16)	C111—C116—H116	119.8
C13—C22—C21	103.94 (15)	C115—C116—H116	119.8
C221—C22—H22	104.1	C15—C151—H15A	109.5
C13—C22—H22	104.1	C15—C151—H15B	109.5
C21—C22—H22	104.1	H15A—C151—H15B	109.5
C13—N24—C25	119.50 (16)	C15—C151—H15C	109.5
C13—N24—C27A	111.13 (15)	H15A—C151—H15C	109.5
C25—N24—C27A	109.14 (15)	H15B—C151—H15C	109.5
N24—C25—C26	104.15 (16)	C226—C221—C222	118.48 (18)
N24—C25—H25A	110.9	C226—C221—C22	124.52 (17)
C26—C25—H25A	110.9	C222—C221—C22	116.99 (18)
N24—C25—H25B	110.9	C223—C222—C221	121.14 (19)
C26—C25—H25B	110.9	C223—C222—H222	119.4
H25A—C25—H25B	108.9	C221—C222—H222	119.4
C25—C26—C27	102.70 (17)	C224—C223—C222	118.92 (19)
C25—C26—H26A	111.2	C224—C223—H223	120.5

C27—C26—H26A	111.2	C222—C223—H223	120.5
C25—C26—H26B	111.2	C223—C224—C225	121.5 (2)
C27—C26—H26B	111.2	C223—C224—Cl24	119.03 (17)
H26A—C26—H26B	109.1	C225—C224—Cl24	119.49 (17)
C27A—C27—C26	101.19 (17)	C224—C225—C226	119.0 (2)
C27A—C27—H27A	111.5	C224—C225—H225	120.5
C26—C27—H27A	111.5	C226—C225—H225	120.5
C27A—C27—H27B	111.5	C225—C226—C221	121.02 (18)
C26—C27—H27B	111.5	C225—C226—H226	119.5
H27A—C27—H27B	109.4	C221—C226—H226	119.5
N24—C27A—C27	105.04 (16)		

C17A—N11—C12—O12	179.86 (18)	C25—C26—C27—C27A	42.0 (2)
C117—N11—C12—O12	−4.6 (3)	C13—N24—C27A—C27	−121.17 (18)
C17A—N11—C12—C13	0.3 (2)	C25—N24—C27A—C27	12.7 (2)
C117—N11—C12—C13	175.81 (17)	C13—N24—C27A—C21	9.2 (2)
O12—C12—C13—N24	−55.7 (3)	C25—N24—C27A—C21	143.07 (17)
N11—C12—C13—N24	123.86 (17)	C26—C27—C27A—N24	−33.6 (2)
O12—C12—C13—C13A	179.83 (18)	C26—C27—C27A—C21	−153.53 (18)
N11—C12—C13—C13A	−0.6 (2)	C34—C21—C27A—N24	130.88 (17)
O12—C12—C13—C22	59.0 (2)	C22—C21—C27A—N24	17.12 (19)
N11—C12—C13—C22	−121.44 (17)	S31—C21—C27A—N24	−109.34 (15)
N24—C13—C13A—C14	59.7 (3)	C34—C21—C27A—C27	−109.5 (2)
C22—C13—C13A—C14	−54.7 (3)	C22—C21—C27A—C27	136.74 (19)
C12—C13—C13A—C14	−176.28 (19)	S31—C21—C27A—C27	10.3 (2)
N24—C13—C13A—C17A	−123.32 (18)	C34—C21—S31—C32	−3.88 (14)
C22—C13—C13A—C17A	122.25 (17)	C27A—C21—S31—C32	−126.91 (15)
C12—C13—C13A—C17A	0.7 (2)	C22—C21—S31—C32	114.09 (15)
C17A—C13A—C14—C15	1.2 (3)	C21—S31—C32—N33	2.99 (16)
C13—C13A—C14—C15	177.86 (19)	C21—S31—C32—S32	−177.52 (14)
C13A—C14—C15—C16	0.7 (3)	S32—C32—N33—C34	179.55 (16)
C13A—C14—C15—C151	−179.08 (19)	S31—C32—N33—C34	−1.0 (2)
C14—C15—C16—C17	−1.8 (3)	C32—N33—C34—O34	179.5 (2)
C151—C15—C16—C17	177.98 (19)	C32—N33—C34—C21	−2.2 (3)
C15—C16—C17—C17A	0.9 (3)	C27A—C21—C34—O34	−51.1 (3)
C16—C17—C17A—C13A	1.0 (3)	C22—C21—C34—O34	58.8 (3)
C16—C17—C17A—N11	−177.57 (18)	S31—C21—C34—O34	−177.70 (18)
C14—C13A—C17A—C17	−2.1 (3)	C27A—C21—C34—N33	130.60 (18)
C13—C13A—C17A—C17	−179.40 (17)	C22—C21—C34—N33	−119.45 (18)
C14—C13A—C17A—N11	176.73 (17)	S31—C21—C34—N33	4.0 (2)
C13—C13A—C17A—N11	−0.6 (2)	C12—N11—C117—C111	110.6 (2)
C12—N11—C17A—C17	178.9 (2)	C17A—N11—C117—C111	−74.5 (2)
C117—N11—C17A—C17	3.4 (3)	N11—C117—C111—C112	−73.7 (3)
C12—N11—C17A—C13A	0.2 (2)	N11—C117—C111—C116	107.8 (2)
C117—N11—C17A—C13A	−175.32 (18)	C116—C111—C112—C113	−0.8 (4)
N24—C13—C22—C221	176.92 (16)	C117—C111—C112—C113	−179.3 (2)
C13A—C13—C22—C221	−60.0 (2)	C111—C112—C113—C114	−0.5 (4)
C12—C13—C22—C221	54.1 (2)	C112—C113—C114—C115	1.3 (4)

N24—C13—C22—C21	41.55 (18)	C113—C114—C115—C116	−0.8 (4)
C13A—C13—C22—C21	164.61 (16)	C112—C111—C116—C115	1.3 (3)
C12—C13—C22—C21	−81.25 (18)	C117—C111—C116—C115	179.8 (2)
C34—C21—C22—C221	71.1 (2)	C114—C115—C116—C111	−0.5 (4)
C27A—C21—C22—C221	−172.48 (16)	C13—C22—C221—C226	−58.1 (3)
S31—C21—C22—C221	−45.4 (2)	C21—C22—C221—C226	71.1 (2)
C34—C21—C22—C13	−152.56 (16)	C13—C22—C221—C222	122.8 (2)
C27A—C21—C22—C13	−36.14 (18)	C21—C22—C221—C222	−108.0 (2)
S31—C21—C22—C13	90.91 (16)	C226—C221—C222—C223	−0.9 (3)
C13A—C13—N24—C25	78.7 (2)	C22—C221—C222—C223	178.21 (18)
C22—C13—N24—C25	−160.02 (16)	C221—C222—C223—C224	0.1 (3)
C12—C13—N24—C25	−37.9 (2)	C222—C223—C224—C225	0.6 (3)
C13A—C13—N24—C27A	−152.79 (16)	C222—C223—C224—Cl24	−177.92 (15)
C22—C13—N24—C27A	−31.52 (19)	C223—C224—C225—C226	−0.5 (3)
C12—C13—N24—C27A	90.62 (19)	Cl24—C224—C225—C226	178.04 (15)
C13—N24—C25—C26	143.31 (18)	C224—C225—C226—C221	−0.4 (3)
C27A—N24—C25—C26	13.9 (2)	C222—C221—C226—C225	1.1 (3)
N24—C25—C26—C27	−34.8 (2)	C22—C221—C226—C225	−178.00 (18)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N33—H33···O12^{i}	0.77 (3)	2.05 (3)	2.811 (2)	170 (3)
C112—H112···S32^{ii}	0.95	2.88	3.760 (3)	155

Symmetry codes: (i) −*x*+1, −*y*+1, *z*+1/2; (ii) −*x*+1, −*y*+1, *z*−1/2.